

# Mesoscopic phase separation in $\text{La}_2\text{CuO}_{4.02}$ - a $^{139}\text{La}$ NQR study

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In crystals of  $\text{La}_2\text{CuO}_{4.02}$  oxygen diffusion can be limited to such small length scales, that the resulting phase separation is invisible for neutrons. Decomposition of the  $^{139}\text{La}$  NQR spectra shows the existence of three different regions, of which one orders antiferromagnetically below 17 K concomitantly with the onset of a weak superconductivity in the crystal. These regions are compared to the macroscopic phases seen previously in the title compound and the cluster-glass and striped phases reported for the underdoped Sr-doped cuprates.

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Inhomogeneous carrier and spin distributions in high- $T_c$  compounds might be related to phase separation and stripes,<sup>1,2</sup> and are intensively studied especially in hole doped  $\text{La}_2\text{CuO}_4$ . In underdoped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  for  $x > 0.06$  doping leads to spin-density wave order or stripe formation, as seen by neutron scattering at various  $x$ -values.<sup>3-6</sup> Recent NQR and NMR studies have revealed new interesting features, like line intensity suppression caused by spin/charge fluctuations, stripe condensation at low temperatures under favorable pinning conditions, and the presence of inequivalent copper sites attributed to a stripe formation.<sup>7-10</sup> At very low Sr content ( $x < 0.02$ ) the magnetic properties are explained in terms of hole segregation,<sup>11-14</sup> and the formation of a cluster spin glass ( $x=0.06$ ).<sup>15</sup>

For  $\text{La}_2\text{CuO}_{4+x}$  the presence of the mobile oxygen dopants leads to a macroscopic structural phase separation in antiferromagnetic (AF) and superconducting (SC) regions in the concentration range  $0.01 < x < 0.06$  (the so called miscibility gap).<sup>16-18</sup> The oxygen mobility is linked to lattice imperfections, e.g. it is strongly increased by the presence of planar defects.<sup>19</sup> In  $\text{La}_2\text{CuO}_{4+x}$  single crystals prepared by the molten solution method<sup>20</sup> oxygen mobility is very low due to the small number of defects and hence the scale of the structural separation can be minimized. The single crystal with  $x = 0.02$  prepared by this way appears homogeneous below 200 K in X-ray and neutron studies,<sup>21</sup> although the composition is inside the miscibility gap. In the crystal a superconducting transition is observed around 15–17 K with a very weak diamagnetic signal.<sup>21,22</sup> According to  $\mu\text{SR}$ <sup>21</sup> part of the sample becomes magnetically ordered below the same temperature of 15 K, but neutron diffraction does not see any long range magnetic structure. Apparently phase separation happens, but the scale is too small to be visible by standard structural methods.<sup>21</sup>

By performing NQR on the same  $\text{La}_2\text{CuO}_{4.02}$  single crystal, we will demonstrate the existence of three regions with different oxygen concentrations and show only one (oxygen-poor) phase to have an antiferromagnetic

transition. We evaluate the size of the antiferromagnetic regions from the reduction of staggered magnetization. By comparison with the macroscopic phases seen previously in the title compound<sup>17</sup> and the cluster-glass and striped phases seen in  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$  and  $\text{La}_{2-x-y}\text{Sr}_x\text{Eu}_y\text{CuO}_4$  we will discuss the influence of the character of the local magnetic order on the NQR spectra.

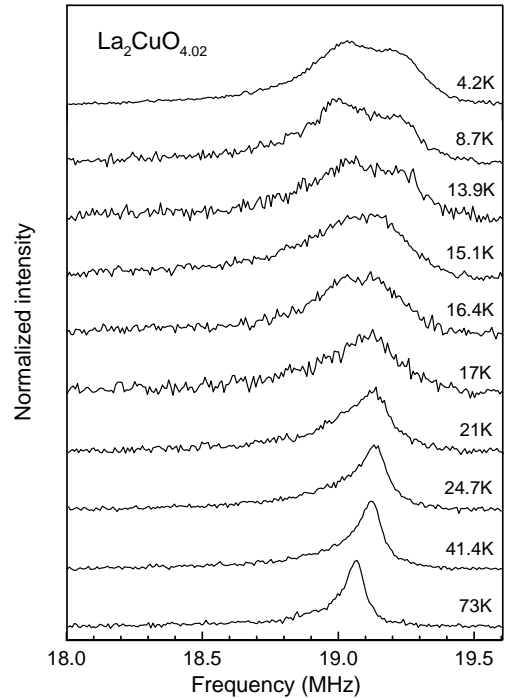


FIG. 1. Normalized  $^{139}\text{La}$  NQR spectra for  $m = 7/2$  at various  $T$ 's in the  $\text{La}_2\text{CuO}_{4.02}$  single crystal.

The  $^{139}\text{La}$  NQR spectra (Figs.1,2) were taken for the  $\pm 7/2 - \pm 5/2$  (referred to as  $m = 7/2$ ) transition by sweeping the frequency. The nuclear spin-lattice relaxation rate  $T_1^{-1}$  (Fig.4) was measured by monitoring the recovery of magnetization after a single  $\pi$  pulse. For

the nuclear spin-spin relaxation (inset of Fig.4) the standard spin-echo decay method was applied. Fig.1 shows the evolution of  $^{139}\text{La}$  spectra with temperature in the  $\text{La}_2\text{CuO}_{4.02}$  single crystal. A lower S/N ratio around 15 K is due to the fast relaxation and partial wipe-out of the signal in this region (see below). Differences in S/N in some adjacent spectra are due to a different number of averages. The central part of the spectrum broadens below 30 K. The splitting of the central line (see also Fig.2b) below 17 K is a manifestation of magnetic ordering of the Cu moments generating an internal magnetic field at the La site. Above the magnetic transition the spectra are well described by the sum of three Gaussian lines (labeled 1, 2 and 3 in sequence of increasing width). Below 17 K the spectra show the same structure but with a splitting of the single narrow line 1 into two lines of equal intensity (1a and 1b) as a result of the AF ordering. Figs.2a,b illustrate the results of a spectral decomposition at 73 K and 4.2 K.

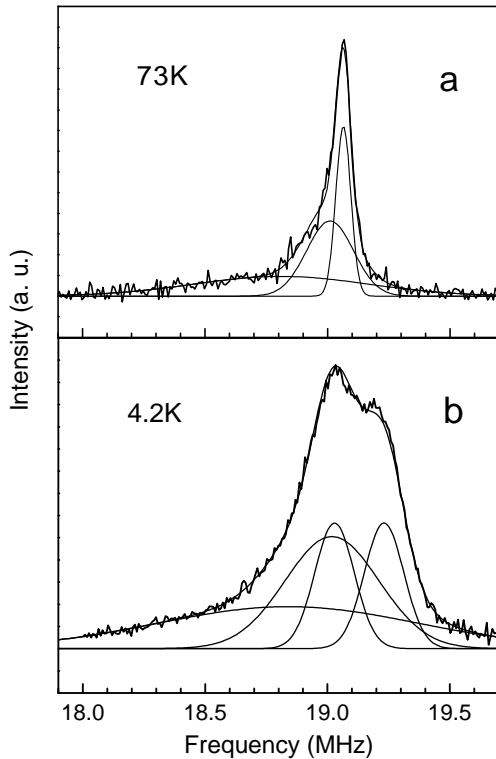


FIG. 2.  $^{139}\text{La}$  spectral decomposition at 73 K and 4.2 K. Due to the antiferromagnetic ordering the narrow line starts to split into two below 17 K.

As already mentioned above, previous experiments showed the possibility of the phase separation.<sup>21</sup> Our NQR spectra are in agreement with this assumption. In addition our data show that separation is present at temperatures much higher than that of the AF transition. We assign the narrow line 1 (Fig.2a) to oxygen-poor (OP) regions, i.e. a phase with low hole doping. This phase is antiferromagnetically ordered below 17 K (two narrow lines in Fig.2b). The broad line (line 3) has to be associ-

ated with oxygen-rich (OR) regions because of its absence in samples with  $x = 0$ . The large width (1 MHz) of this line is due to the distortion of the electric field gradient at the La site because of the presence of holes in the  $\text{CuO}_2$  planes leading to the distribution of the oxygen octahedral tilts and the bond lengths.<sup>17,23</sup> The OR regions are likely responsible for the superconductivity. The hole concentration in the  $\text{CuO}_2$  planes does not depend on the method of doping, which allows a comparison to the line position data for La in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ <sup>24</sup> (to see the similarity with the copper data in ref.[ 10], one has to realize that extra holes shift the Cu resonance up, while lowering the La frequency<sup>25</sup>). In  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  the line positions at 4.2 K obey the relation  $\nu = (19.15 - 5x)$  MHz. Using this expression and a hole to excess oxygen ratio of 2:1, the line positions at 4.2 K of 19.13 MHz (midpoint of lines 1a and 1b), 19.02 MHz and 18.84 MHz give oxygen concentrations of 0, 0.01 and 0.035 for lines 1, 2 and 3 resp. The  $x$  dependence of  $T_c$  in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ <sup>14</sup> gives an independent way to estimate the hole concentration in the OR-regions. In the phase diagram superconductivity is suggested to start around 0.06.  $T_c = 15$  K gives a hole concentration in the OR phase near 0.07 or excess oxygen concentration of 0.035, in agreement with the value found above. In the macroscopically phase separated sample, the oxygen concentration in the OR phase is 0.06.<sup>17,18</sup> This concentration difference is not surprising since due to the restricted oxygen mobility the local oxygen concentrations will be far from their equilibrium values. According to the above given evaluation, line 2 belongs to regions with rather low oxygen content, although it shows no sign of antiferromagnetic ordering. This line possibly arises from the interface between OP and OR regions and might be compared to the relatively narrow and weak line observed in macroscopically phase separated  $\text{La}_2\text{CuO}_{4.035}$  besides the broad metallic and splitted narrow antiferromagnetic lines.<sup>17</sup> In our case the weight in the spectrum will be enhanced due to the small sizes of the correlated regions.

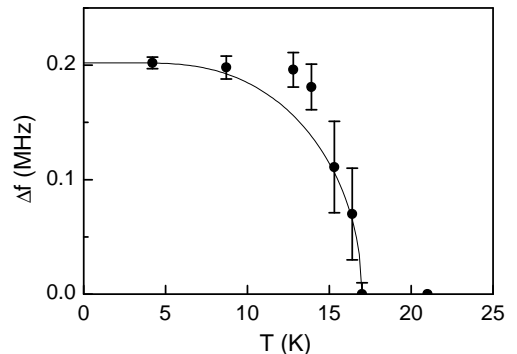


FIG. 3.  $^{139}\text{La}$  NQR line 1 splitting for  $m = 7/2$  vs.  $T$ . Drawn line is the mean field staggered magnetization for  $S=1/2$  ( $T_N=17$  K,  $\Delta f(0)=202$  kHz).

The splitting of the line 1 is almost  $T$  independent from 14 K to 4.2 K (see Fig.3) and just below the ordering tem-

perature  $T_{AF} = 17.0 \pm 0.5$  K seems to increase somewhat faster with lowering  $T$  than the mean field behavior of the staggered magnetization for  $S=1/2$  (drawn line on Fig.3). The line splitting (200 kHz) and hence the internal field at the La-site at 4.2 K is 20% lower than the 250 kHz splitting in antiferromagnetic undoped  $\text{La}_2\text{CuO}_4$ .<sup>26</sup> This means a 20% reduction of the staggered magnetization and an ordered magnetic moment, that is  $0.43 \mu_B/\text{Cu}$  instead of  $\langle \mu \rangle = 0.48 \mu_B/\text{Cu}$  in the undoped compound. In the SDW-like AF ordered striped phase of the Eu and Sr doped compound this value is  $0.29 \mu_B/\text{Cu}$ .<sup>10</sup> A temperature dependent reduction of the staggered magnetization in the system with low Sr doping has been explained by finite size effects<sup>27</sup> caused by microsegregation of the holes in domain walls of flat domains.<sup>11,13</sup> At low temperatures this effect vanishes due to the hole localization. In our case local field reduction is observed even at 4.2 K and may be explained as a finite size effect caused by a small grain dimension. At  $T = 0$  K the staggered magnetization of a domain of size  $L$  (infinite in the two other directions) drops by 20% for  $L$  about 20 lattice spacings (8 nm).<sup>13</sup> For a quasi-two-dimensional domain (due to the large anisotropy) the reduction should increase and hence this value has to be considered as a lower limit. The neutron data<sup>21</sup> place an upper limit of the same order of magnitude. Thus an average grain size of the order of 8 nm looks reasonable and confirms phase separation on a mesoscopic rather than macroscopic scale.

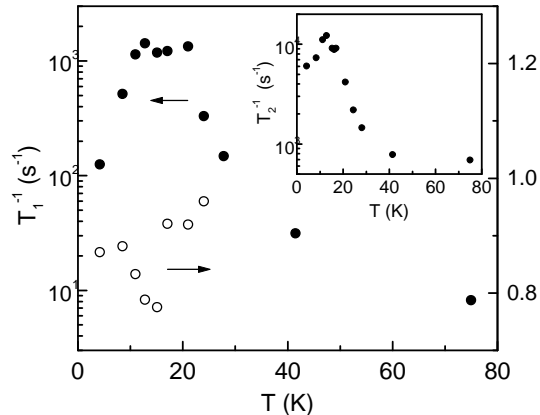


FIG. 4.  $^{139}\text{La}$  spin-lattice relaxation rate vs.  $T$ . Closed circles – fast contribution, open circles – relative value of the fast contribution (scale on the right).  $T_1$  (slow) is of the order of 0.1 s. Inset:  $^{139}\text{La}$  spin-spin dephasing rate vs.  $T$ .

The  $T$  dependencies of the spin-lattice ( $T_1^{-1}$ ) and spin-spin ( $T_2^{-1}$ ) relaxation rates are illustrated in Fig.4 and its inset. Both rates show a large peak at low temperatures. Near the peak temperature, the nuclear magnetization recovers after the initial magnetization reversal ( $M_z(t)$ ) in case of  $T_1^{-1}$ , or the loss of transversal magnetization ( $M_x(t)$ ) in case of  $T_2^{-1}$ , are characterized by stretched exponential time dependencies  $\exp[-(t/T_{1,2})^\alpha]$ .<sup>28</sup> Very close to the maximum, fits of  $M_z(t)$  require a slow and fast time constant. For both  $T_1$ 's  $\alpha$  is about 0.5, while the

quality of the  $M_z(t)$ -fit is found to depend only weakly on the precise value for  $T_1$  (slow) (of the order of 0.1 s). Closed circles in Fig.4 show the temperature dependence of the fast rate. Below 17 K there is a sharp decrease of this contribution (open circles in Fig.4).

The strong growth of the  $^{139}\text{La}$  relaxation rates around 15 K is explained as a result of hole localization and slowing down of hole mediated spin fluctuations.<sup>9,12</sup> Here in the same temperature region the AF and SC transitions occur. The coincidence of these phenomena likely leads to even more complicated behavior of nuclear relaxation rates, e.g. the above mentioned decrease of the fast contribution to the longitudinal relaxation just below 17K (Fig.4). The occurrence of slow and fast contributions to  $M_z(t)$  is typical for a multiphase material. Further analysis is not pursued, as its precise character might not only depend on the AF transition alone, but on the co-existing SC transition as well. The other feature caused by the low temperature relaxation behavior is a partial wipe-out of the La NQR signal in the same temperature region. The total intensity multiplied by  $T$  and corrected for the echo decay factor (Fig.5) shows a decrease around 15 K by about a factor 3 indicating part of the nuclei to have dephased before the echo signal could be measured.<sup>9</sup> The relative decrease of the intensity of the narrow line (1) starts below 70 K (inset of Fig.5) and becomes very pronounced below 30 K. It demonstrates a difference in relaxation behavior in the OP and OR phases. The imprint on other NQR features, if any, might be limited to the changes in the stretched exponential recoveries (see above).

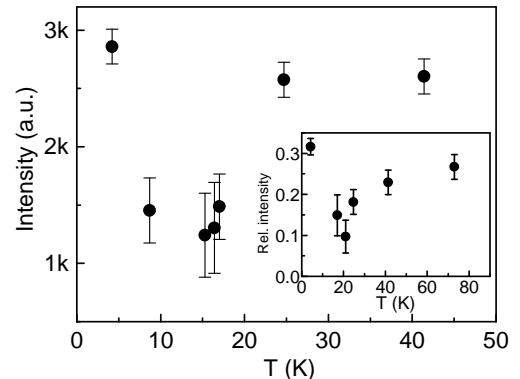


FIG. 5. Corrected intensity of the  $^{139}\text{La}$  spectrum vs.  $T$ . Inset: Relative intensity of the narrow line vs.  $T$ .

How do these results compare to those in the low doped Sr-cuprates? In  $\text{La}_{1.94}\text{Sr}_{0.06}\text{CuO}_4$ <sup>15</sup> the La spectra (NMR and NQR) show the existence of at least two sites below 200 K, of which one site is ascribed to AF clusters. The change in the La NMR spectrum around 20 K seems to signal glass formation. Wipe-out effects are clearly seen for Cu-NMR but no La-NQR wipe-out data are shown. In  $\text{La}_{1.48}\text{Sr}_{0.12}\text{Nd}_{0.4}\text{CuO}_4$  La wipe-out is found to be almost complete.<sup>29</sup> In  $\text{La}_{2-x-y}\text{Sr}_x\text{Eu}_y\text{CuO}_4$  with  $0.08 < x < 0.18$ , Cu-NQR shows the presence of three inequivalent sites,<sup>10</sup> which is also reminiscent to our

case. At low doping at 1.3 K the Cu-intensity is strongly reduced compared to a  $x = 1/8$  sample due to wipe-out effects without affecting the relative strengths of the three lines. This comparison shows at least three major differences of the NQR spectra: in  $\text{La}_2\text{CuO}_{4.02}$  wipe-out effects on the La-site are less severe, and mainly linked to the relaxation peak and the antiferromagnetic transition below 17 K, line features are much sharper than in the Sr-doped cuprates, and the line splitting (hence internal field) in the AF state is almost the same as in the undoped case. The large wipe-out values over very extended temperature regions of the Sr-doped samples seem to be typical for mobile striped or glassy phases, which are not expected in our compound.

The most intriguing feature is the coincidence of the AF and superconducting transitions in the investigated single crystal.<sup>21</sup> The AF ordering temperature is very low in comparison with  $T_N$ 's of macroscopically phase separated  $\text{La}_2\text{CuO}_{4+x}$  samples, which are usually higher than 200 K.<sup>18</sup> The transition is sharp (Fig.3) and it looks as the AF state is strongly depressed at high temperatures and is triggered by some reason at low temperatures (the above mentioned relaxation behavior below 17K supports this assumption). It has been argued that superconductivity itself destabilizes the homogeneous metallic state and leads to the formation of (super)conducting droplets weakly linked to each other and separated by insulating (antiferromagnetic) regions.<sup>30</sup> Our system is already inhomogeneous above the AF and SC transitions because the oxygen phase separation occurs at much higher temperatures but the hole concentration in OR grains is far from optimal. Therefore the occurrence of superconductivity in the OR grains might cause an additional electronic redistribution, which favors the AF transition in the OP grains. The other possibility is that both antiferromagnetism and superconductivity are triggered by a common mechanism e.g. slowing down of spin fluctuations coupled to hole motion occurring in the same temperature region.

In summary in single crystal of  $\text{La}_2\text{CuO}_{4.02}$  with limited oxygen mobility the three different La sites seen by NQR are associated with oxygen-poor, oxygen-rich and intermediate regions reminiscent the O-doped macroscopically separated system and the Sr-doped glassy or striped  $\text{La}_2\text{CuO}_4$  compounds. Sharper lines, well defined transition temperatures, internal fields close to bulk values and less severe wipe-out effects are seen as the main difference of the NQR data with low Sr-doped cuprates instead of O-doping. The evaluated OP grain size of the order of 8 nm shows that the crystal is phase separated on a mesoscopic scale. Although, like in the undoped high- $T_c$  systems, superconductivity itself is not directly reflected in the NQR data, some features of the antiferro-

magnetic transition in the OP phase (a sharp transition at low temperature with  $T_N \sim T_c$  and  $^{139}\text{La}$  relaxation peculiarities) are indicative for a possible coupling with the superconducting transition in this system.

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